Short communication

Hydrogen production by methanol–water solution electrolysis with an alkaline membrane cell

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HIGHLIGHTS

► The concept of methanol–water solution electrolysis with an alkaline membrane.
► Alkaline environment is an attractive alternative to the conventional electrolysers.
► The system is capable to operate with a high efficiency.
► Increased temperature enhances the hydrogen production.

ABSTRACT

The basic concept of methanol–water solution electrolysis with an alkaline membrane and the experimental studies are presented. The measurements were performed with a membrane electrode assembly consisting of an anion exchange membrane, Pt/C cathode and either PtRu/C or Pt/C anode. Hydrogen production efficiency was measured and the effects of temperature and methanol concentration on the electrolysis performance were investigated. PtRu was found to be a better catalyst at low potentials and the hydrogen was produced with a high efficiency. The results indicate that the favored kinetics and mass transport at high temperatures result in increased hydrogen production. Additionally, it was found that, increasing methanol concentration decreased the performance of the electrolysis as the membrane morphology changes as a function of the concentration.

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1. Introduction

Hydrogen is considered as one of the most promising energy carriers for future electrical devices owing to its environmentally friendly production possibilities and high energy density. There are various methods for hydrogen production but electrolysis is the most suitable for on-site production, e.g. producing hydrogen for mobile or transportable electrical devices using fuel cells, although it is not limited by the size of the applications and can be also utilized for industrial hydrogen production as well. Water electrolysis is the conventional form of electrolysis but the energy consumption is high and therefore an interest for hydrogen production by methanol electrolysis has arisen due to various advantages over conventional water electrolysis [1–5]. The standard potential of methanol electrolysis is only 0.02 V which is

significantly lower than 1.23 V of water electrolysis resulting in decreased power consumption, though in practice the operation voltage of methanol electrolysis is above 0.4 V [1,3,5] and that of water electrolysis above 1.4 V [6–8]. The cost for long term hydrogen production by water electrolysis for large-scale applications is mainly determined by the energy consumption as the cost of electrolysis equipment becomes insignificant. It has been estimated that the energy saving with methanol electrolysis can be about 70% compared to water electrolysis and when the production costs of methanol is taken into account methanol electrolysis is expected to be 50% cheaper than water electrolysis [9].

When considering a small scale portable application also the expense of the equipment is relevant. Electrolysis is closely related to fuel cells and one important area in the fuel cell research has been finding cheaper materials and techniques to manufacture the cells. For instance, the costs of Nafion® proton exchange membranes are high due to the complicated manufacturing process and thus anion exchange membranes provide a possibility for a significant decrease in the electrolyte price. Another reason to

investigate alkaline membrane cells is the enhanced methanol oxidation kinetics in alkaline media [10,11] enabling decreased catalyst loadings and there is even a possibility to utilize non-precious metal catalysts for methanol oxidation [12–14]. Furthermore, methanol cross-over from an anode to a cathode in the Nafion membrane methanol electrolysers increases fuel consumption generating impurities in the produced hydrogen and consequently, membranes have been developed further to overcome this problem [15–17]. Anion exchange membranes, however, are more resistant towards methanol cross-over, for example a Fumapem® FAA-2 membrane has a cross-over rate only 16% of that of the Nafion-115 membrane [18].

In this paper the basic concept of methanol–water solution electrolysis with an alkaline membrane is introduced. In addition, experimental studies with this electrolysis method, including efficiency measurements, were performed and the effects of temperature and methanol concentration on the electrolytic performance are presented.

2. Methanol–water solution electrolysis with an alkaline membrane

A scheme of methanol–water solution electrolysis with an alkaline membrane is shown in Fig. 1: the electrolytic cell is composed of an anode, a cathode and an anion exchange membrane electrolyte placed between the electrodes. Supported metals are used as the electrocatalysts on both electrodes which are connected to each other through an electrical circuit via a DC power source. Methanol–water solution is fed to the anode where methanol is oxidized in a reaction with hydroxide ions transferred through the anion exchange membrane. The products at the anode are carbon dioxide, water and electrons according to Eq (1). The electrons are circulated to the cathode through the DC power source.

$$CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^- \tag{1}$$
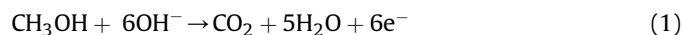
$$E_a^0 = 0.81 \text{ V vs. SHE}$$

Water is transported through the membrane to the cathode where it is reduced releasing hydrogen gas and forming hydroxide ions according to Eq. (2). Hydroxide ions are transported through the anion exchange membrane to the anode compartment.
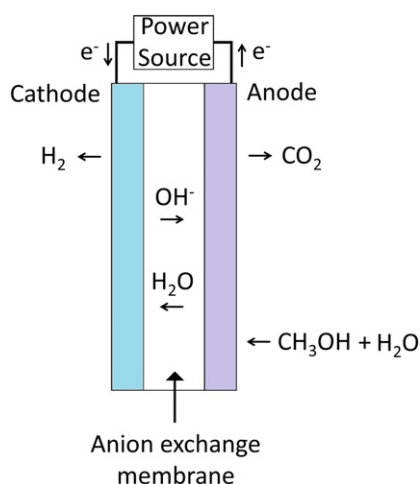
$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{2}$$

$$E_c^0 = -0.83 \text{ V vs. SHE}$$

The resulting overall reaction for the methanol–water solution electrolysis is expressed in Eq. (3).

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \tag{3}$$

$$E^0 = -0.02 \text{ V}$$

It is crucial that no oxygen is present at the cathode in order to avoid the more advantageous fuel cell type reaction displacing hydrogen evolution.

3. Experimental

Carbon supported Pt catalyst (60% Pt/C, Alfa Aesar) was used as the cathode catalyst and either carbon supported Pt-Ru alloy (40% Pt − 20% Ru/C, Alfa Aesar) or the aforementioned Pt/C as the anode catalyst. The catalyst ink was prepared by mixing the catalyst with a 2:1 solution of isopropanol and water, and it was ultrasonicated in a water bath for 30 min to form a homogeneous mixture. Alkaline ionomer polyvinylbenzyltrimethylammonium (PVBTA) (MW 100 000) from Scientific Polymer Products Inc. and divinylbenzene (DVB) cross-linker from Merck were mixed into a 2:1 solution of isopropanol and water, and heated in a boiling water bath for 15 min to activate the polymerization. Catalyst ink and polymer solution were mixed together followed by heating for 15 min in a boiling water bath prior to painting the ink. A Fumapem® FAA-2 anion exchange membrane by FuMa-Tech used was used as the solid electrolyte. The membrane electrode assembly (MEA) was made by spraying catalyst ink onto both sides of the membrane. After painting, the MEA was dried in a vacuum oven at 60 °C for 60 min and subsequently hot pressed for 120 s at 30 MPa and 80 °C. The MEA, with geometric electrode area of 7.29 cm^2 and catalyst loading of 0.5 mg cm^{-2} at both electrodes, was ion exchanged to hydroxide form by treating it 24 h in a 0.5 M NaOH solution. The cell was assembled by sandwiching the MEA between gas diffusion layers and polytetrafluoroethylene gaskets backed up by graphite blocks with serpentine flow field channels and finally clamped together with eight bolts that were tightened with a torque of 10 Nm.

The cell was stabilized overnight both before starting the measurements and after changing the fuel concentration. In order to measure the difference between Pt and PtRu catalysts at the anode, the cell performance was analyzed with both catalysts. The hydrogen production rates at various current densities were analyzed by measuring the gas flow volume from the cathode outlet, and the performance of the methanol electrolysis was analyzed at different temperatures and methanol concentrations. The cell was controlled by an Autolab PGSTAT20 potentiostat (Metrohm) equipped with a BSTR10A booster. All the potential sweeps were performed with a low sweep rate, 0.5 mV s^{-1}, to ensure stable conditions through the potential scale.

4. Results and discussion

Methanol oxidation has shown enhanced activity on PtRu alloy catalysts [11,19,20] and therefore the performance of the electrolyser with a 1 mol dm^{-3} methanol solution was studied with Pt and PtRu catalysts at 30 °C temperatures (Fig. 2a). In low potential region (<1.2 V) the PtRu catalyst provides a higher performance in comparison to Pt due to a higher resistance to CO poisoning as CO oxidation from catalyst surface occurs at lower potentials on the PtRu surface than on pure Pt [21]. However, at high potentials
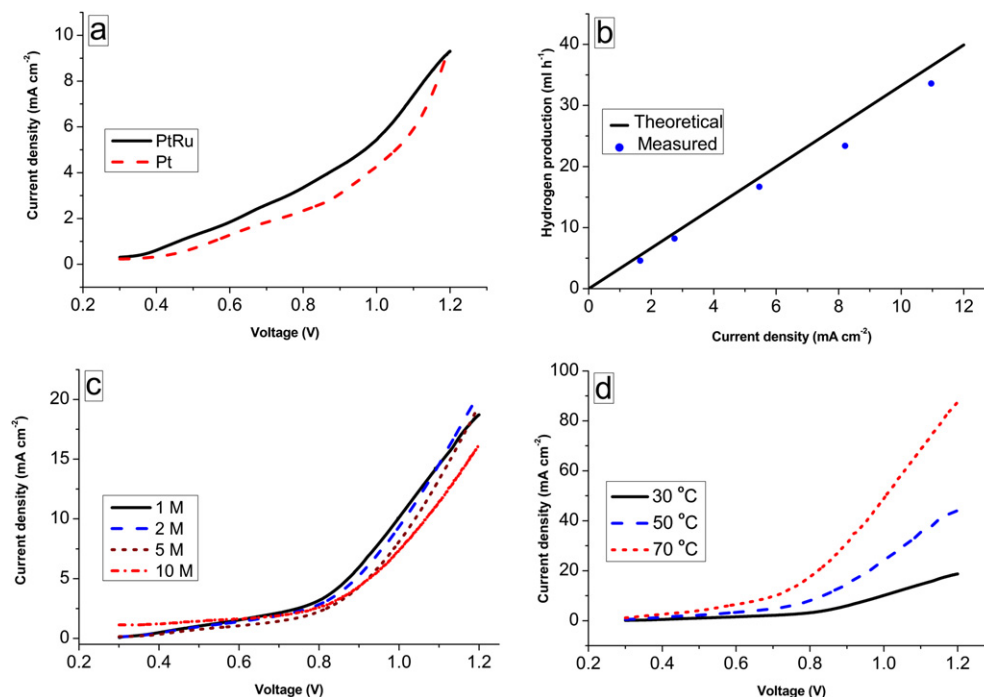

Fig. 1. Schematic of methanol–water solution electrolysis with an alkaline membrane.

Fig. 2. Comparison of Pt and PtRu anode catalysts at 30 °C with 1 mol dm^{-3} methanol (a), hydrogen production rate dependency of the current density (b), the effect of fuel concentration at 30 °C (c) and the effect of temperature with 1 mol dm^{-3} methanol (d).

(>1.2 V) the obtained current with the Pt catalyst approaches the current observed with PtRu because at these potentials water also dissociates on pure Pt sites enabling CO oxidation and moreover the density of active sites towards methanol oxidation is higher in the pure Pt catalyst. Nevertheless, for real applications the lower potential region is of interest and therefore PtRu was selected as the catalyst for further studies.

The dependency of the hydrogen production rate on current density has been studied in order to verify the current efficiency of the electrolysis (Fig. 2b). The almost linear hydrogen production rate, which is close to a theoretical amount, shows that the electrolytic cell performs with a high efficiency reaching values higher than 90%.

Electrolysers are preferred to be operated with a concentrated fuel in order to minimize the required fuel volume and therefore the effect of methanol concentration was studied at 30 °C (Fig. 2c). Fuels with a concentration of 1 and 2 mol dm^{-3} perform very similarly but with concentrations of 5 and 10 mol dm^{-3} the performance decreases. This phenomenon results from the changes in the membrane morphology and properties as it has been reported [22] that the membrane swells and the ion conductivity decreases when methanol concentration increases. In addition, the self-diffusion coefficient of water in the membrane is lower with 10 mol dm^{-3} methanol than in the studied solutions with lower concentrations. These changes explain the differences obtained in the electrolysis with varying methanol concentrations. Moreover, methanol cross-over increases with higher concentrations and although methanol does not react at the cathode, the cross-over increases fuel consumption and methanol can vaporize as an impurity in the produced hydrogen.

The effect of concentration has been studied also at higher temperatures and similar kinds of behavior with slight differences were obtained: 1 and 2 mol dm^{-3} fuels showed comparable performance at all the temperatures. At 50 °C and 70 °C there is an evident drop in the performance with the 5 and 10 mol dm^{-3} methanol solutions compared to the fuels with low concentration, even though at 30 °C only slightly weaker performance was obtained with the high concentration fuels, and currents obtained with the 5 mol dm^{-3}

methanol even exceeded those with 1 mol dm^{-3} methanol at high voltages. The morphology of the membrane is assumed to change at the elevated temperatures resulting in changes in transportation which explains the obtained expanding gap between various concentrations when temperature is increased.

Polarization of the alkaline membrane electrolyser has been studied at temperatures of 30 °C, 50 °C and 70 °C with 1 mol dm^{-3} methanol as a fuel and the results are shown in Fig. 2d. It can be clearly seen that the current densities rise with increasing temperature. At 1 V potential the currents are 10.1 mA cm^{-2}, 24.0 mA cm^{-2} and 48.9 mA cm^{-2} at temperatures of 30 °C, 50 °C and 70 °C, respectively. This phenomenon is similar to that observed with direct methanol fuel cells [23] as the increased temperature enhances mass transport and reaction kinetics resulting in reduced activation and concentration overpotentials. This behavior also has been reported previously for methanol electrolysers utilizing acidic membranes [1,4] although the obtained currents with alkaline membrane are lower. One reason for this is the significantly lower catalyst loadings in the studied electrodes (0.5 mg cm^{-2}) compared to those used with acid electrolyzers (3 mg cm^{-2} [1], anode 2.5 mg cm^{-2} and cathode 1.5 mg cm^{-2} [4]). The other reason is the order of magnitude lower ion conductivity of the FAA-2 membrane compared to Nafion 115 [23] as the electrolyte resistance increases the required electrolysis overpotential. In addition, it can be seen that the onset potentials decreases with increasing temperature and the onset potentials are approximately 0.72 V, 0.70 V and 0.65 V at temperatures of 30 °C, 50 °C and 70 °C, respectively. The high overpotential required for the electrolysis is due to the sluggish electrode reactions. The onset potentials for acidic electrolysers have been lower than these [1,3,4] which reflects the different methanol oxidation reaction mechanisms and kinetics between alkaline and acidic environment. Although alkaline environment has shown enhanced methanol oxidation kinetics the anion exchange membrane as such may not be enough alkaline to support this effect but would require addition of an alkaline salt in the fuel.

5. Conclusion

The concept of methanol–water solution electrolysis in a fuel cell equipped with an alkaline membrane for hydrogen production is introduced, offering the possibility for lower power consumption in hydrogen production when compared to traditional water electrolysis. The alkaline membrane electrolyser is an attractive alternative to the conventional electrolysers with proton exchange membranes enabling the utilization of low-cost membrane materials offering savings with material expenses.

PtRu was found to be a better catalyst than Pt for methanol oxidation in alkaline electrolysis cell in low potential region ($<$1.2 V). The system is capable to operate with a high current efficiency producing almost the theoretical amount of hydrogen and the efficiency increases with increasing current which is essential for real applications.

Increasing methanol concentration resulted in decreased performance in the electrolysis due to morphological changes in the membrane structure resulting in a decreased ion conductivity and water self-diffusion coefficient. The results indicate that the membrane requires improvements before operating the cell with a highly concentrated fuel to minimize the needed fuel volume for practical applications.

This novel method opens a new area for investigation in hydrogen production and enables alternative material choices to produce commercially viable methanol electrolysers although further development is required.

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